

COMPUTATIONAL STUDY OF IONIC LIQUID SOLVATION.

J.O. Ellison and M.P. Heitz*

Department of Chemistry, The College at Brockport SUNY, Smith Hall, 350 New Campus Drive, Brockport, NY 14420

Ionic liquids are of particular interest because they offer an “environmentally friendly” alternative to volatile organic hydrocarbon (VOC) solvents. One principle of green chemistry promotes the use of innocuous solvents in chemical processing. The overall goal of our research is to determine the solvation energetics of ionic liquids when dissolved in conventional solvents such as methanol (MeOH) and water. The ionic liquids used in this work are based on the trihexy(tetradecyl)phosphonium ($P_{[14,6,6,6]}^+$, PIL) and 1-decyl-3-methylimidazolium ($C_{10}MIM$) cations. To date we have studied the solvation of PIL with chloride and bromide anions and $C_{10}MIM$ with the chloride anion. The PIL and $C_{10}MIM$ systems were modeled computationally using Spartan14® software using different levels of theory and basis sets, including AM1, PM3, and PM6 semiempirical methods and Hartree Fock ab initio methods with 3-21G and 6-31G basis sets. Solvation was computed using continuum dielectric solvents with SM5.4 and SM8 solvent models. The optimum cation/anion separation (energy minimum) was determined by calculating the interaction energy in both vacuum and dielectric continuum. In vacuum PIL-Cl has an optimum separation of 0.359 nm compared to PIL-Br which has an optimum separation of 0.365 nm, consistent with the trend in anion radius. The optimum distance for $C_{10}MIM$ -Cl was found to be 0.268 nm in vacuum. Solvation energies of solvated ion pairs and solvent separated ions were computed for all solvents studied and are discussed in this work.